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PARTICULARS OF STRUCTURAL CHANGES IN POROUS GLASS UNDER THE ACTION OF LASER RADIATION DURING 'COLD' THERMAL COMPACTION

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An attempt at local modification of the optical properties in the interior of macroporous glass plates with porosity 0.58 cm^3/cm^3 and average channel size 50 – 70 nm by means of laser radiation weakly absorbed in the material is reported. The source of radiation is an ytterbium fiber laser with radiation wavelength $\lambda = 1.07$ μm, pulse duration $\tau_p \sim 100$ nsec and pulse repetition frequency $\nu = 10 – 100$ kHz. The temperature and the power of the radiation passing through of the irradiated region versus the duration of the exposure are presented.

Key words: modification in the interior of glass, porous glass, laser irradiation, 'cold' compaction.

One of the main directions of growth of modern laser technologies is the creation of modified regions (MR) with altered optical properties in glass and glass-ceramic materials [1, 2]. The possibility of creating MR with a complex structure in the interior of optical materials and preserving functionality and quality of the MR created over long periods of operation is being intensively studied. The capability of MR to localize, reflect and refract as well as focus or scatter incident radiation makes it possible to find a wide range of applications of MR as functional micro-optic elements in rapidly developing areas of optoelectronics, integrated optics and photonics [3].

As a rule, laser radiation with ultrashort pulses ($\tau_p = 10^{-9} – 10^{-15}$ sec), high repetition frequency ($\nu = 100 – 250$ kHz) and long wavelength ($\lambda = 0.8$ μm) is used to create MR with a complicated structure in optically transparent materials [1, 2, 4 5]. Owing to the high power density ($q = 10^{10} – 10^{15}$ W/cm^2) nonlinear absorption of the incident radiation is possible in the region of focusing of the laser radiation, which gives rise to local heating and thermal change of the structure, i.e., the formation of a region with altered optical properties. A change in the optical properties of the region can be manifested as a change in the refractive index n [4] or absorptive power A of the material [5] as well as in the appearance of a crystal structure [2] or nonlinear optical susceptibility [6]. Such technologies make it possible to form MR with extended shape in the interior of the material, which can be regarded as waveguide structures [1, 5, 6].

The trends in the development of laser technologies for forming MR in the interior of a material transparent to radiation for forming MR are a reduction of the laser power density to $10^4 – 10^5$ W/cm and switching to long pulse durations ($10^{-6} – 10^{-9}$ sec) or, as reported in [7 – 9], to continuous-wave radiation. These trends are based on the search for and development of new promising materials, one of which is porous glass (PG) [7 – 9]. The advantages of PG over other optical materials are high thermal and radiation resistance and the possibility of regulating the parameters of the PG framework, which comprises a complicated, highly extended structure consisting of many channels and pores. These characteristics of PG make this material very promising for use in modern laser technologies for forming MR.

Porous glass plates are obtained by removing a chemically unstable borate phase during treatment in a 3 M HCl solution at temperature 100°C followed by careful washing in distilled water and drying at 100°C for 1 h. Cavities in the form of a branching system of channels and pores with average diameter 2 – 7 nm are formed at locations from which dissolved components of a chemically unstable phase are removed. A very small amount of silica present in the dissolved phase remains in the channels of the PG in the form of a finely dispersed gel. In the terminology of S. P. Zhdanov such glass is said to be microporous (MIP) [10].

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MIP-glass plates additionally treated in a 0.5 M solution of KOH at 20°C, as a result of which the fine amorphous silica is completely removed from the cavities of the silica framework, are said to be macroporous (MAP) [10]. The average size of the cavities freed of fine amorphous silica and equal to the size of the channels in MIP glass was 50 – 70 nm for the glasses used in the experiment.

It was demonstrated in [7 – 9] that MR with a complicated structure can form in the interior of MIP-glass plates under irradiation by continuous-wave laser radiation with wavelength weakly absorbed in the plate material. The experimental evaluation of the absorptive power of a plate of ‘dry’ MIP glass turned out to be $A = 0.004$. Such a low absorptive power of PG plates indicated that the process resulting in the formation of MR is nonthermal. Studies of the optical characteristics of the MR formed in the interior of PG plates also indicated indirectly that the refractive index increases inside structures created in the process of ‘cold’ thermal compaction under the action of laser irradiation [11].

The evaluations of the increase in the temperature t at the center of the region of irradiation performed in [12] using a relation presented in [13] also indicated that the MR formation process in nonthermal. This relation describes the interaction of radiation at constant power with the weakly absorbing material:

$$t = \frac{AP_{\text{inc}}}{4\pi\rho ch\alpha} \ln\left(19.4 \frac{\alpha\tau}{r_0^2}\right) + t_0, \quad (1)$$

where τ is the duration of the action of the laser radiation, r_0 is the size of the beam waist, h is the penetration depth of the light in the material, ρ is the density, c is the specific heat of the PG plates, P_{inc} is the power of the incident radiation and A is the absorptive power.

For $A = 0.004$ the temperature at the center of the irradiated region rose by 1 – 2°C.

The experimental studies of the increase in temperature recorded at the center of the irradiated region during the entire irradiation time showed that the temperature increase falls within the error range of the measurements [12].

In [7, 9] it was assumed that the process leading to the formation of MR in the interior of a MIP-glass plate under the action of laser radiation which is practically not absorbed by the plate material could be associated with the mass transfer of the fine amorphous hydrated (by water molecules) silica lining the walls of the channels in the silica framework. The mass transfer occurs inside the irradiated region from the periphery into the central part of the MR, where the secondary constant electric field is strongest. The constant electric field is due to the polarization of the molecules of substances filling the channels in the PG.

To check the supposition of mass transfer, in [13] MIP-glass plates were permeated, before irradiation, with a high-polarizability substance — glycerin. The absorptive power A of the glycerin-permeated MIP-glass plates determined from the experimental data using the method of [9] during the action of the laser radiation was, on average, 0.06 – 0.11 [13]. The maximum temperature recorded in the experiment during the formation of the MR at maximum power of the incident continuous-wave radiation from an ytterbium fiber laser (wavelength $\lambda = 1.07$ μm, 16.5 W) did not exceed 100°C. Thermal compaction of the PG plated at 100°C was unlikely to occur, since appreciable changes in the dimensions of plates during sintering in a furnace start at temperatures above 750°C. Thus, this experimental fact indicates that the formation of MR based on thermal processes is unconvincing.

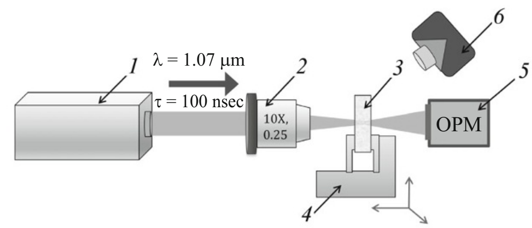

Fig. 1. Experimental arrangement: *1*) pulse fiber ytterbium laser; *2*) microscope objective; *3*) x-y table; *4*) MAP-glass plate; *5*) detector in the optical power meter (OPM); *6*) thermal imagery camera.

In the present article the supposition that the process resulting in the formation of MR by mass transfer of substances present in the channels of the PR, first and foremost, fine amorphous silica, which is the ‘building’ material of the MR formed, is checked. The laser-induced local action occurs on a MAP-glass plate from whose channels the fine amorphous silicon was completely removed.

EXPERIMENTAL PART

The experiment with MAP-glass plates was performed on the setup shown schematically in Fig. 1. This setup contains the following: a pulsed ytterbium fiber laser *1* with wavelength weakly absorbed in the material; microscope objective (×10, 0.25) *2*; x-y table *3*, on which the MAP-glass plate *4* is secured; an optical power meter (OPM) *5*; and, a TV camera *6*.

The coordinate (x–y) table can be moved with accuracy ±1 μm along the optical axis. The MAP-glass plates with porosity $\delta = 0.58$ cm^3/cm^3 and channel radius 50 – 70 nm were fabricated at the I. V. Grebenshchikov Institute of Silicate Chemistry of the Russian Academy of Sciences (IKhS RAN). The composition of the plates was (mass fraction, %): 96.0 SiO_2 – 3.5 B_2O_3 – 0.3 Na_2O. MAP-glass plates with the dimensions 15 × 15 × 1.5 mm were used in the experiment.

Plates of ‘dry’ MAP glass were used in one of the experiments. The second experiment was performed on an MAP-glass plate permeated with liquid with a high polarizability — distilled water (1.86 D). The plates were permeated in 72 h. Thirty minutes before the start of the experi-

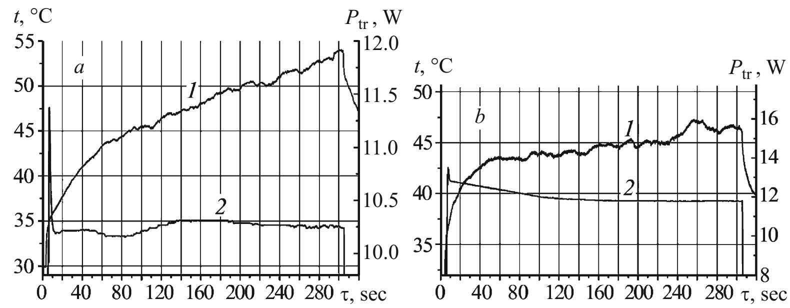

Fig. 2. Transmitted radiation power P_{tr} and temperature t in the irradiation region versus the interaction time τ: *a*) for 'dry' MAP glass; *b*) for MAP glass permeated with water; *1*) temperature, °C; *2*) power.

ment the plate was removed from the permeating liquid and dried with filter paper.

The 'dry' MAP-glass plate and the MAP-glass plate permeated with water were exposed to radiation from the ytterbium fiber laser with wavelength $\lambda = 1.07$ μm, pulse duration $\tau_p \sim 100$ nsec and pulse repetition frequency $\nu = 100 - 250$ kHz; the radiation power was varied in the range 12 – 20 W. The exposure time in all experiments was 300 sec, since MR were formed at precisely this frequency in MIP-glass plates and in MIP-glass plates permeated with glycerin by using a continuous-wave laser module with wavelength $\lambda = 0.8$ μm, spectral width $\Delta\lambda = 1$ nm, average power $P = 120$ mW and linear polarization of the beam. To form MR in glycerin-permeated MIP-glass plates using pulsed radiation the formation time of the MR determined in the present work was much shorter and equal to 90 sec [13]. The microscope objective with magnification ×10 and numerical aperture 0.25 created in the laser beam a waist of size $d = 25$ μm in the interior of the plate at depth 200 – 300 μm.

The power of the laser radiation transmitted through the MAP plate (P_{tr}) was recorded with a Gentec Solo-2M OPM with an UP19K-110F-H9 pyroelectric power detector with measuring accuracy 1% and equivalent noise power about 1 mW. A Flip Titanium 520 M television camera with size resolution in the measured region 30 × 30 μm and measurement accuracy 25 mK in the temperature interval 20 – 300°C was used in the experiment. The temperature of the MAP-glass plates in the region of the waist of the laser radiation was recorded throughout the entire experiment.

The transmission spectra for the MIP- and MAP-glass plates used in the experiment on MR formation were obtained using an MSFU-KYU-30.5.54.072 microscope-spectrophotometer.

DISCUSSION

Examining the dependence of P_{tr} on the exposure time τ (Fig. 2*a*) one can see immediately that the radiation power transmitted through both plates did not change with time. This probably indicates the absence of any change in the optical properties of MAP-glass, specifically, the absorptive power and the refractive index during the action of the radiation in the region of the waist of the laser beam. The formation of MR, which consists of a change in the optical properties of glass, was not observed, which most likely indicates the absence of mass transfer of matter in the region of the waist. This experimental fact indirectly confirms the supposition that the formation of MR is due to laser-induced mass transfer of matter present in the channels of the PG. The absence of fine amorphous silica in the channels of the MAP-glass plate and the absence of MR formation at the end of the irradiation process under the condition that the irradiation time is much longer than the time characteristic for the formation of MR in MIP-glass plates shows that the process leading to the formation of MR is mainly due to the mass transfer of matter within the region of focusing.

The higher values of the power in studying the dependence of the transmitted power P_{tr} on the irradiation time τ (Fig. 2*b*) for water-permeated MAP-glass as compared with 'dry' MAP-glass plates are probably associated with the fact that greater scattering by channels emptied of fine amorphous silica is characteristic for 'dry' MAP-glass plates than in water-permeated MAP-glass plates, where the lesser scattering by channels is due to the smaller difference in the refractive indices of the MAP matrix ($n_{MAP} = 1.46$) and water ($n_w = 1.333$). Depending on the temperature changes as a function of the irradiation time this difference should be manifested in a smaller increase of the temperature for water-permeated MAP-glass plates as compared with 'dry' MAP-glass plates (see Fig. 2*b*).

As concerns the dependence of the increase in temperature on the irradiation time τ, we have a monotonic increase in both cases, which is seen clearly for 'dry' MAP-glass plates, which is consistent with the explanations presented.

In evaluating the temperature increase at the center of the irradiated region by means of the expression (1) for 'dry' MAP-glass plates and water-permeated MAP-glass plates we have encountered the fact that there is no information on the thermal conductivity and specific heat of MAP-glasses. For this reason, the calculations were performed using the values of the specific heat and thermal conductivity presented in [14], while the density was calculated using the well-known relation $\rho = f(\delta)$ from [15].

The values of the absorptive power of 'dry' MAP-glass plates A_1 and water-permeated MAP-glass plates A_2 were determined using the experimental results obtained by the procedure described in [9]: $A_1 = 0.17$ and $A_2 = 0.08$. The values

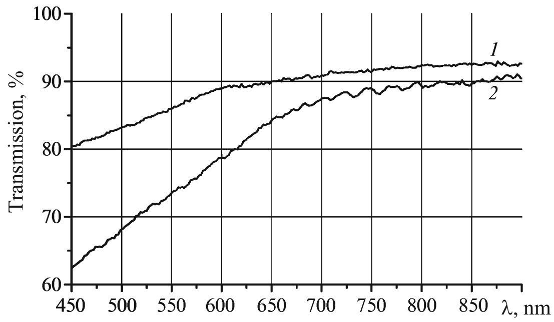

Fig. 3. Transmission spectrum of MIP-glass (*1*) and MAP-glass (*2*) plates in the wavelength range 400 – 900 nm.

of the temperature increase for A_1 and A_2 were found to be $\Delta t_1 = 90°C$ and $\Delta t_2 = 50°C$.

For 'dry' MAP-glass plates the computed values of Δt_1 are significantly greater than the experimentally measured values.

For water-permeated MAP-glass plates the values of Δt_1 and Δt_2 are in satisfactory agreement.

The difference in the results of calculations and the experiment on determining the increase in the temperature at the center of the irradiated region in 'dry' MAP-glass plates can be explained by the fact that the losses due to scattering in this glass cannot be neglected in determining A_1. Taking account of the losses due to scattering σ in calculating A_1 would necessarily decrease its value and thereby decrease the value of Δt_1.

There is no information in the literature on the losses due to scattering for MAP-glass plates with porosity $\delta = 0.58$ cm^3/cm^3, though data on the dependence of the light transmission on the wavelength of the incident radiation in the wavelength range 350 – 800 nm for MAP-glass plates with close composition and data analysis with porosity $\delta = 0.56$ cm^3/cm^3 and thickness 1.8 mm are available [15].

It is evident from the wavelength dependence of the transmission of MIP- and MAP-glasses (Fig. 3) that the transmission of MAP-glass plates in the entire experimental range is lower than in MIP-glass plates. The difference in the transmission of these plates is greatest in the wavelength range 350 – 400 nm and decreases with increasing wavelength, but the character of the dependence nevertheless makes it possible to suppose that it remains the same for wavelength $\lambda = 1.07$ μm. The value of the transmission coefficients of both plates in the entire experimental range correlates with the values presented in [16].

CONCLUSIONS

The constancy of the laser radiation power transmitted through the irradiated region as a function of the exposure time is characteristic for 'dry' plates as well as water-permeated MAP-glass plates used in the experiment and indicates that the optical properties, specifically, the absorptive power and the refractive index within the region of focusing, remain unchanged during irradiation. The absence of any changes in the optical properties of both MAP-glass plates in the irradiated region shows that the formation of MR did not occur. This experimental fact is indirect confirmation of the fact that the process resulting in the formation of MR is due to mass transfer of matter present in the channels in PG and is initiated by the action of the laser radiation.

The smaller temperature increases recorded experimentally as compared with the computed values for 'dry' MAP-glass plates are probably due to the fact that in the calculation of the absorptive power of this PG the scattering by channels emptied of the fine amorphous silicon cannot be neglected.

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